Synopsis of proposed Ph.D. research work

Title of the proposed thesis:

Synthesis of ceramic oxides from metal-organic precursors and investigation of their properties

by

Debamalya Ghosh

Registration No.- VB-530 of 2011-12

Roll No. - Ph.D. (C.W.) Sik-22

DEPARTMENT OF CHEMISTRY
SIKSHA-BHAVANA (INSTITUTE OF SCIENCE)
VISVA-BHARATI UNIVERSITY
SANTINIKETAN-731235
WEST BENGAL
INDIA

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1. Origin of the research problem

In modern days' metal oxides have been the subject of extensive investigation due to their optical, electronic, mechanical, thermal, magnetic and other related properties.[1-8] The properties are exploited in many technological applications such as ferrofluid, biomedicine, photocatalysis and high-density data storage.[9-17] The synthesis of such oxides phases have been effected using many approaches, *viz*., sol-gel,[18] combustion synthesis,[19-22] coprecipitation,[23] high-energy ball-milling,[24-26] thermal plasma synthesis,[27] hydrothermal method,[28] rapid quenching[29] and spray pyrolysis of metal nitrate solutions.[30]

Metal-Organic precursor[31-39] for the preparation of solids is attractive as it provides excellent control over the stoichiometry. Such precursor phases can also lead to the formation of solids with crystallite sizes in the nano-regime. The formation of ceramic silicates from aluminosilicate zeolites, by a catalytic addition of a simple oxide to the zeolite precursors is an important development. The precursor to solid ceramic oxide phase transformation may not be a simple single step process, but can go through other intermediate phases, which could either be crystalline or amorphous. The formation of pure mixed oxide phase, generally, requires heating at temperatures in excess of 1000 °C. The precursor method, however, provides a route by which ceramic oxide phases could be prepared at reasonable temperature, which is due to the atomic level mixing of the elements in a well characterized crystal structure. This approach has been well exploited in solid state chemistry; *viz*., the synthesis of $BaTiO_3$ from the barium titanyl oxalate precursor. The metal-organic framework compounds, possess both versatility and diversity in their structures, which could be profitably exploited as a precursor for the preparation of mixed metal oxides. This route could also lead to the formation of nano-sized mixed metal oxides, which could be of considerable technological interest.

Thus, the focus of this research proposal will be to design metal organic framework compounds with appropriate topology and metal ions ratio which can be used as single source precursors for the

formation of complex ceramic oxides. The strategy will be to use lower temperature for the transformation studies of network compounds to oxides materials so that particle size of the materials will be in nano-regime. However, based on our preliminary investigations, we have discovered that it is more fruitful to employ the metal-organic framework compounds which have two geometrically different metal ions (with same coordination number) or two metal ions with different coordination numbers.

2. Objectives of the work

1. To design and synthesis of metal-organic framework compounds with two different metal ions.
2. To synthesize the ceramic oxides using mixed metal-organic framework compounds as precursors.
3. To study the stability of the mixed metal framework compounds for fine-tuning of the decomposition temperature for the synthesis of oxide materials in nano-regime.
4. To characterize the materials in terms of shape, particle size, surface area etc.
5. To investigate the properties of the mixed metal oxide materials such as magnetism, photoluminescence, sensing, photo catalysis, electrical and other advanced applications.

3. Methodology

1. Synthesis of metal-organic framework precursors using low temperature hydrothermal technique and sol-gel method.
2. Determination of the structure of the synthesized compounds using single crystal X-ray diffraction (SCXRD) if the structure is new (based on the data of PXRD).
3. Characterizations of the metal-organic network compounds using powder X-ray diffractions (PXRD), IR, SEM, EDX, UV-Vis etc.

4. After the structure determination of the metal-organic networks (using PXRD or SCXRD), it will be ready to use as precursor if we get appropriate metal ion ratio to synthesize mixed metal oxides ceramic materials.
5. The thermal transformation studies will be carried out using the metal-organic framework compounds to synthesize the ceramic oxides materials.
6. As synthesized materials (after thermal treatment) will be characterized using powder X-ray diffractions. If we get the target ceramic materials, the X-ray data will be indexed and refined using traditional methods. The temperature and time of the thermal treatment will be tuned to prepare different sized ceramic oxides materials. If we achieved to prepare nano-structures with different sizes, these materials will be reproduced for further investigation (various size dependent properties).
7. If we able to prepare the pure materials, then the oxide materials will be characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), EDX etc.
8. We will study UV-Vis, luminescence based sensing of the desired oxide materials.
9. Magnetic properties of the oxide materials will be studied by VSM, PPMS instruments

4. Future Prospect

The metal-organic networks with infinite structures are comparatively new types of compounds and the research in this field have been popularized in the last 15 years. Most of the works in this area are based on the synthesis of new porous network compounds and the uses of these materials in the area of gas storage, separation, magnetic materials, luminescent materials, drug delivery etc. The uses of these materials as single source precursor for the synthesis of inorganic materials are beginning to emerge. For the hope of new light, our future effort will be to study the morphology of different oxides and fine thermal tuning of their sizes from the macro to nano-regime by choosing the suitable metal-organic precursor. To go further, we will further investigate their properties like

magnetism, luminescent, sensing, electrical and catalytic properties of different sized nano-structured materials will be studied and sized dependent variation of these properties will be analyzed. The effort paves the way for the future applications in devices based on metal oxide nanostructures such as nano-lasers, field-effect transistors, solar cells, sensors and so on. The future achievements inspire more enthusiasm of researchers to overcome the challenges that remain.

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